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Experiments on the Kinetics of Oxygen Transport from Oxide Fuel to the Clad Related to GCFR Fuel Pins*

by

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Abstract

The reaction of the oxygen of mixed oxide fuels with the cladding material can be divided roughly into three subsequent steps, which correspond to three single processes in the solid and gaseous phases. Each of these steps can be the rate controlling process.

In this paper preliminary experiments, which give an insight into the oxygen transport and allow to estimate the rate controlling single process, will be described and discussed.

It resulted, that the oxydation of the clad is rate controlling. Oxygen transport from $(U_{0.8}Pu_{0.2})O_{2-x}$ to the clad via the gas phase disappears at O/M ratios ≤ 1.96. The diffusion coefficient of oxygen in hypostoichiometric uranium-20 mol % cerium-mixed oxide, which was used in the experiments, was estimated to be $2 \cdot 10^{-8}$ cm^2/sec at 1050°C.

Zusammenfassung

Die Reaktion des Sauerstoffs aus dem Mischoxid Brennstoff mit der Hülle kann angenähert in drei aufeinanderfolgende Schritte aufgeteilt werden, die den Einzelprozessen in den festen und gasförmigen Phasen entsprechen. Jeder der drei Schritte kann die Reaktionsrate bestimmen.

In dieser Arbeit werden vorläufige Experimente, die einen Einblick in den Sauerstofftransport geben und erlauben den geschwindigkeitsbestimmenden Einzelprozeß zu finden, beschrieben und diskutiert. Es wurde festgestellt, daß die Sauerstoffaufnahme der Hülle die Reaktionsrate bestimmt. Der Sauerstofftransport von $(U_{0.8}Pu_{0.2})O_{2-x}$ zur Hülle wird bei O/M-Verhältnissen ≤ 1.96 unbedeutend. Für den Diffusionskoeffizienten von Sauerstoff in unterstöchiometrischem Uran-20 mol % Cer-Mischoxid, das bei den Experimenten verwendet wurde, ergab sich $2 \cdot 10^{-8}$ cm^2/sec bei 1050°C.

I. Introduction

Uranium-plutonium mixed oxide is considered to be a suitable fuel for pin-type gas cooled fast breeder reactor. Therefore the kinetics of oxidation of cladding materials at temperatures prevailing in fuel pins is of interest. Comparing the mixed oxides with the uranium dioxide, we find a much lower oxygen affinity; that is so also in the hyperstoichiometric state of the mixed oxide due to the presence of plutonium oxide. This is a disadvantageous property of the fuel, which leads to an oxidation of cladding materials with high oxygen affinities as shown recently by experiments with vanadium alloys [1]. These former experiments and considerations of the oxidation processes gave no indication wether the equilibrium state will be reached during the irradiation period of the fuel pins. It is now the object of this paper to gain a better understanding of the kinetics of oxidation of cladding materials by mixed oxide fuels.

The reaction of the oxygen of mixed oxide fuels with the cladding material can be divided roughly into three subsequent steps, i.e. three single processes which are attributed to the different states of the oxygen during the reaction. Each of these steps can be the rate controlling process.

The first step is the release of oxygen from the mixed oxide fuel. This process depends on the diffusion of oxygen in the solid matrix of the

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mixed oxide and on the surface of the fuel determined by cracks and open porosity.

The second step is the transport of oxygen in the gas phase along cracks and interconnected pores and through the peripheral gap. This process depends on both the partial pressures of oxygen and of the carrier gases and the diffusion rate of the gases in the existing atmosphere.

The third step is the penetration of oxygen into the cladding material, which depends on the partial pressure of oxygen in the gas phase, on processes within the boundary layer of the gas phase and the clad and on the diffusion of oxygen into the cladding material.

In this paper preliminary experiments will be described and discussed which give an insight into the effective oxygen transport processes and allow to estimate the rate controlling single process. The experiments were performed with uranium cerium mixed oxide specimens with 20 mol% of cerium oxide instead of uranium plutonium mixed oxide, because the former can be easily handled. With regard to the object of our study this is reasonable since the oxygen has nearly the same behaviour in both mixed oxide systems. A V3Ti1Si alloy was taken to be the cladding material with relatively high affinity to oxygen. The alloy and the mixed oxide specimen were heated together within a closed silica glass tube containing a defined atmosphere to study the oxygen release from the mixed oxide, the transport via the gas phase and the penetration into the alloy material.

II Experiments

1) Oxygen release from the fuel

The first step of the reaction is controlled by diffusion of the oxygen from the interior of the mixed oxide fuel through the solid matrix and along the grain boundaries to the surface of the fuel. To investigate this process the experimental conditions must be adjusted in the way that diffusion through the mixed oxide matrix is the rate controlling process.

A fuel disk of 6mm diameter and 0.5mm thickness and an alloy specimen were enclosed together in a small silica glass tube and heated up to 1050°C. In the chosen form the fuel specimen represents the peripheral part of a reactor fuel pin, which has an average temperature of 1050°C and is decisive for the rate of oxygen release by solid state diffusion. The silica tube contained an argon-hydrogen gas mixture which acts as carrier gas for oxygen by formation of water. In order to get an effective oxygen transport via the gas phase, the partial pressure of hydrogen was set high enough to secure the partial pressure of water not to drop below 0.1 Torr during the experiment. As the surface of the alloy specimen was sufficiently large, the rate of oxygen transport was determined only by the rate of oxygen release from the surface.

The oxygen release of the fuel disk was estimated by determination of the change in weight of both, the mixed oxide and the alloy specimen. Fig 1 shows the variation of the oxygen to metal ratio of the cerium component in the mixed oxide and the increase in weight of the alloy specimen as a function of the heating time. It depicts the development of oxygen release from the mixed oxide, which was controlled by solid state diffusion. The equilibrium O/Ce ratio of 1.74 which was established already after 20 hours of heat treatment, had been determined by the oxygen potential of the silicon dioxide of the tube. After equilibration of the O/Ce ratio the oxidation of the vanadium alloy continued due to the beginning reduction of the silicon dioxide. From the O/Ce curve in Fig 1 a diffusion coefficient of

$$D = 2 \cdot 10^{-8}\ \mathrm{cm}^2/\mathrm{sec}$$

was calculated for the oxygen release from the mixed uranium-cerium oxide with 20 mol% of cerium at 1050 °C.

II 2) Oxygen transport via the gas phase

The second step of the reaction, the transport via the gas phase is controlled by both the partial pressure of water and the rate of gas diffusion.

To secure the gas transport being the rate controlling process in the experiment, fine grained CeO_2 powder and powdered alloy material were enclosed together in the silica glass tube and heated up to 800 °C. The gas within the tube was 1 at of argon, containing 10 vpm hydrogen. Thus the partial pressure of hydrogen in the tube was as low or lower than that in a fuel pin of a helium cooled reactor. The helium in a reactor contains at least 1 vpm of hydrogen which penetrates the cladding wall.

The time at which the equilibrium O/Ce ratio had been attained was determined from the change in weight of the cerium oxide powder again. Fig 2 shows the change in the O/Ce ratio as a function of time. The equilibrium ratio of 1.73, which is determined by the oxygen potential in silicon dioxide as well, is reached already after 5 hours of heat treatment. Fig 2 also depicts the increase in weight of the powdered alloy caused by oxidation. The oxidation of the alloy continued after equilibration of the cerium oxide due to reduction of the silicon dioxide by the alloy. However the oxidation rate became much lower in this stage since the partial pressure of water dropped below 10^{-4} Torr.

II 3) Oxidation of the cladding alloy

The third step of the reaction is controlled by the oxygen partial pressure in the gas phase, by processes in the surface layer and by the diffusion rate of oxygen within the alloy.

In the experiment CeO_2 powder was used to spend oxygen for the oxidation of the alloy disk, hence the absorption of oxygen and its penetration into the alloy became the rate controlling process. The ratio of cerium oxide and alloy material was about the same as in a fuel pin. A disk of 6mm diameter and 1mm thickness of the alloy had been used in the experiment which was performed again in a silica glass tube at 800°C with 1 at of argon containing 10 vpm hydrogen. The oxidation of the alloy was estimated by determination of the increase in both the weight and the hardness of the alloy disk as shown in Fig 3. The quasi equilibrium between the alloy and the CeO_2 powder is attained after some 100 hours at an O/Ce ratio of 1.73 and an oxygen content of 5 At.% in the alloy specimen. In the beginning the oxidation rate was very high. In the following stage it became lower according to the decrease of the oxygen partial pressure in the gas phase.

The change in hardness as a function of the distance of the surface of the alloy specimen (cf.Fig 3) shows the distribution of oxygen in the interior. After 143 h a nearly homogeneous distribution of oxygen is reached. A protective layer had not been formed.

III Conclusions

The reaction between uranium cerium mixed oxide and the V3Ti1Si alloy gives an example of the development of the reaction between a mixed oxide fuel and the cladding material. The experiments show that in the range of O/Ce ratios 2 to 1.7 equilibrium is reached between the mixed oxide and the alloy already after 150 hours. It resulted that the oxidation of the alloy specimen was the rate controlling process in the reaction. Due to the decrease in the oxygen potential during the reaction the oxygen transport via the gas phase became rate controlling at O/Ce ratios of about 1.75 where the vapor pressure of water in the argon atmosphere had reached 10^{-4} torr. The transport disappears at vapor pressures below 10^{-5} torr.

The consideration of the oxidation of the alloy can be applied only to the special case of vanadium alloys, while the study of the release of oxygen from the mixed oxide and the transport via the gas phase allows to give an indication of the rates of both processes in an uranium-plutonium fuel pin in the reactor with any cladding material.

The process of oxygen release may develop more slowly in uranium plutonium than in uranium cerium mixed oxides, but will not prevent an equilibration of the oxygen potentials in an reactor fuel pin. An estimation of the diffusion coefficient of oxygen in hypostoichiometric uranium plutonium mixed oxide, which is in progress, will allow a more complete discussion.

The knowledge of the oxygen potential in uranium plutonium mixed oxide allows us to estimate the O/Pu ratio at which the gas transport of oxygen disappears, i.e., no appreciable amounts of oxygen migrate via the gas phase to the clad. For this purpose we must take into account the partial pressure of hydrogen in a fuel pin, which is caused by the impurities in the helium cooling gas. In highly purified helium the hydrogen impurity is about 1 vpm. Since the hydrogen penetrates the cladding wall, it causes a partial pressure of 0.1 torr in the fuel pin, if we assume a cooling gas pressure of 100 at. The experiments reveal that gas transport of oxygen disappears if the partial pressure of water drops below 10^{-5} torr. Since in reactor pins the distance between fuel and clad is only about 10 µm, instead of a few millimeter in the experiment, the limiting vapor pressure of water will be some 10^{-7} torr in a fuel pin. With this vapor pressure a H_2O/H_2 ratio of 10^{-6} is estimated which corresponds with an O/Pu ratio of 1.8 in the mixed oxide. Hence in a fuel with 20 mol% of plutonium oxide no appreciable oxygen transport takes place via the gas phase below an O/Pu ratio of 1.8, i.e. an O/M ratio of 1.96.

References

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Kerntechnik 14. (1972), 8, 347-53.

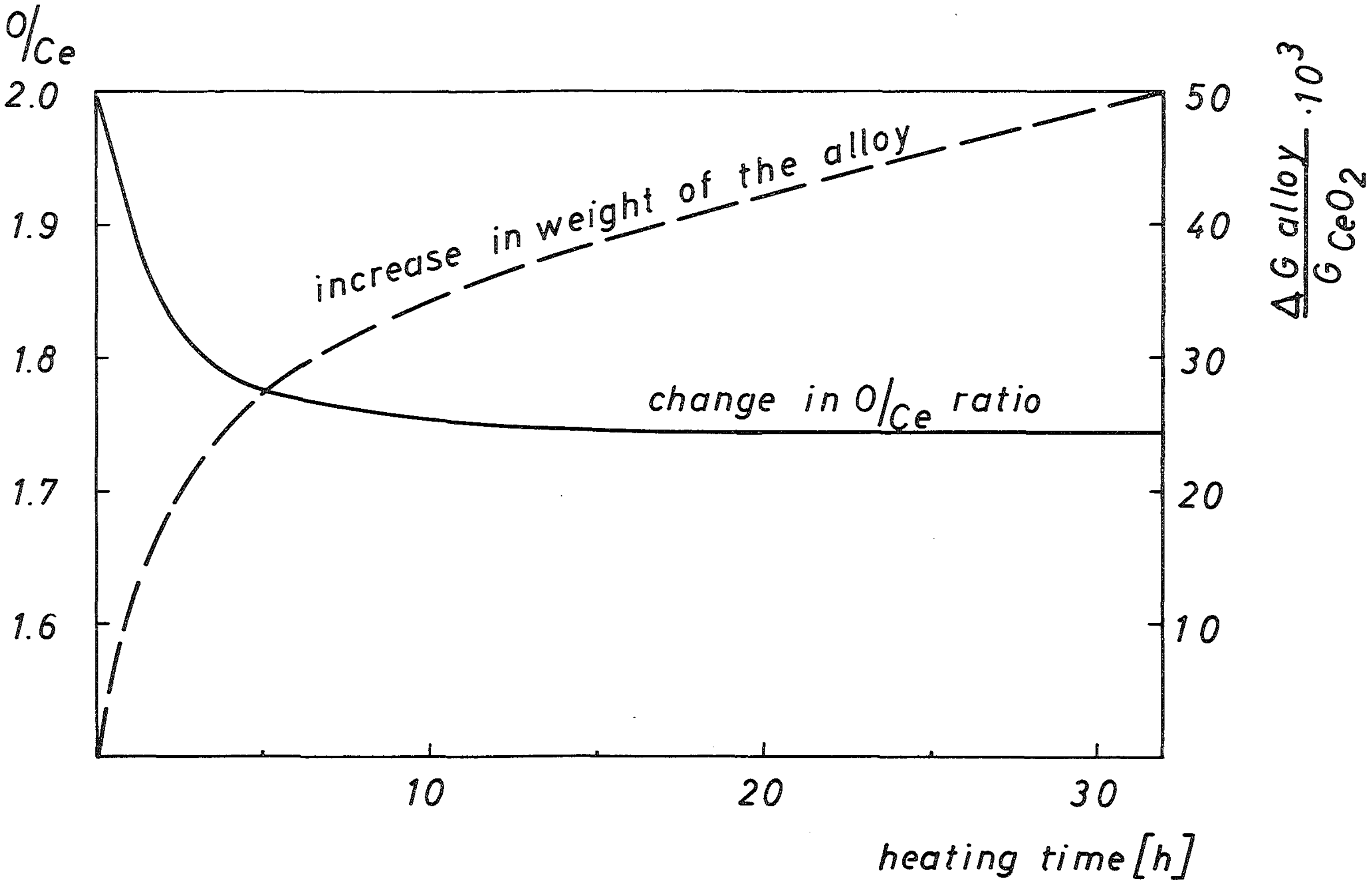

Fig. 1 Change in the O/Ce ratio of $(U_{0.8}Ce_{0.2})O_2$ mixed oxide pellets and increase in weight of the V3Ti1Si-alloy during the reaction at 1050°C in argon-hydrogen atmosphere.

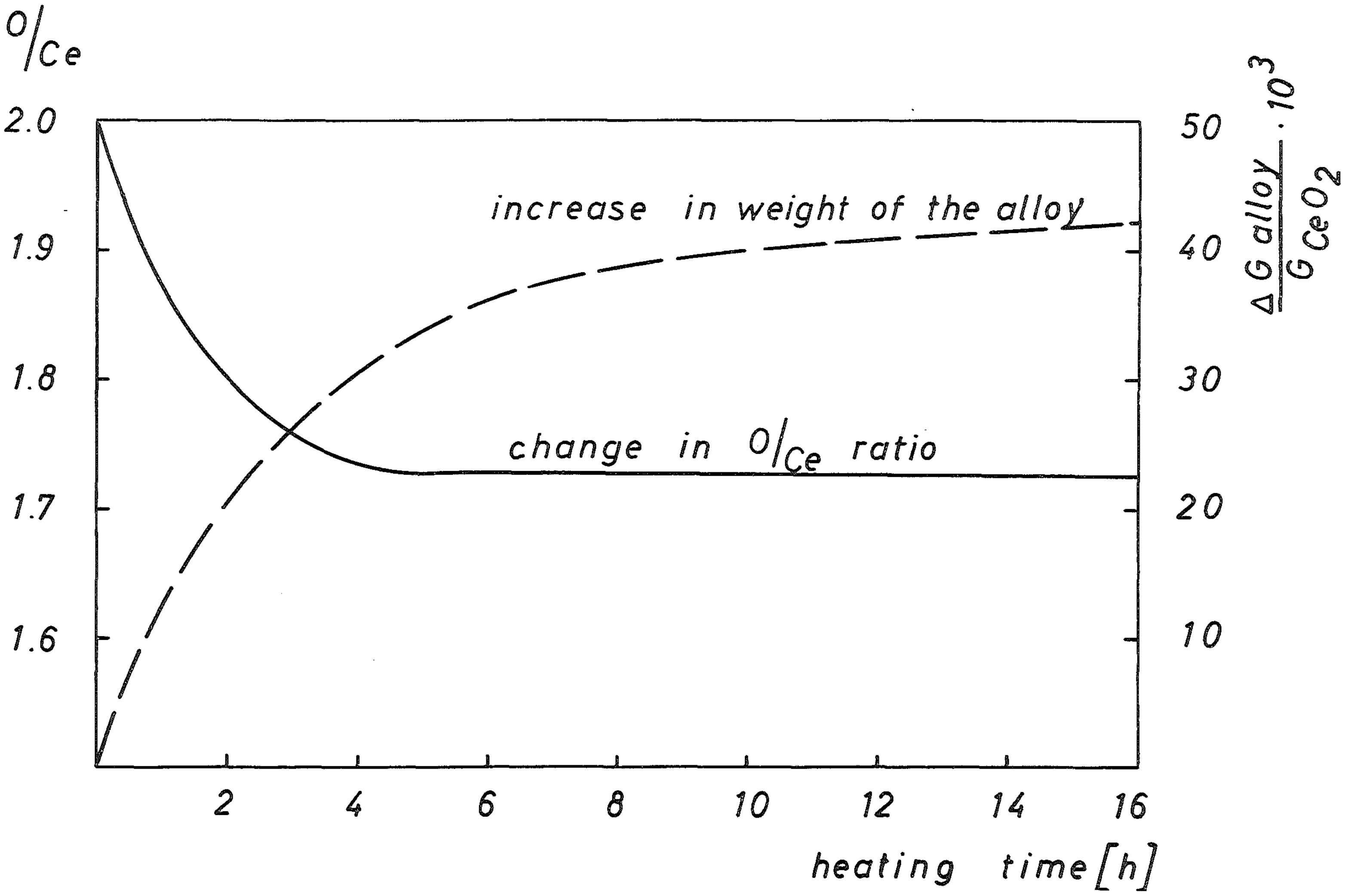

Fig. 2 Change in the O/Ce ratio of CeO_2 powder and increase in weight of the V3Ti1Si powder during the reaction at 800°C in argon atmosphere containing 10 vpm hydrogen.

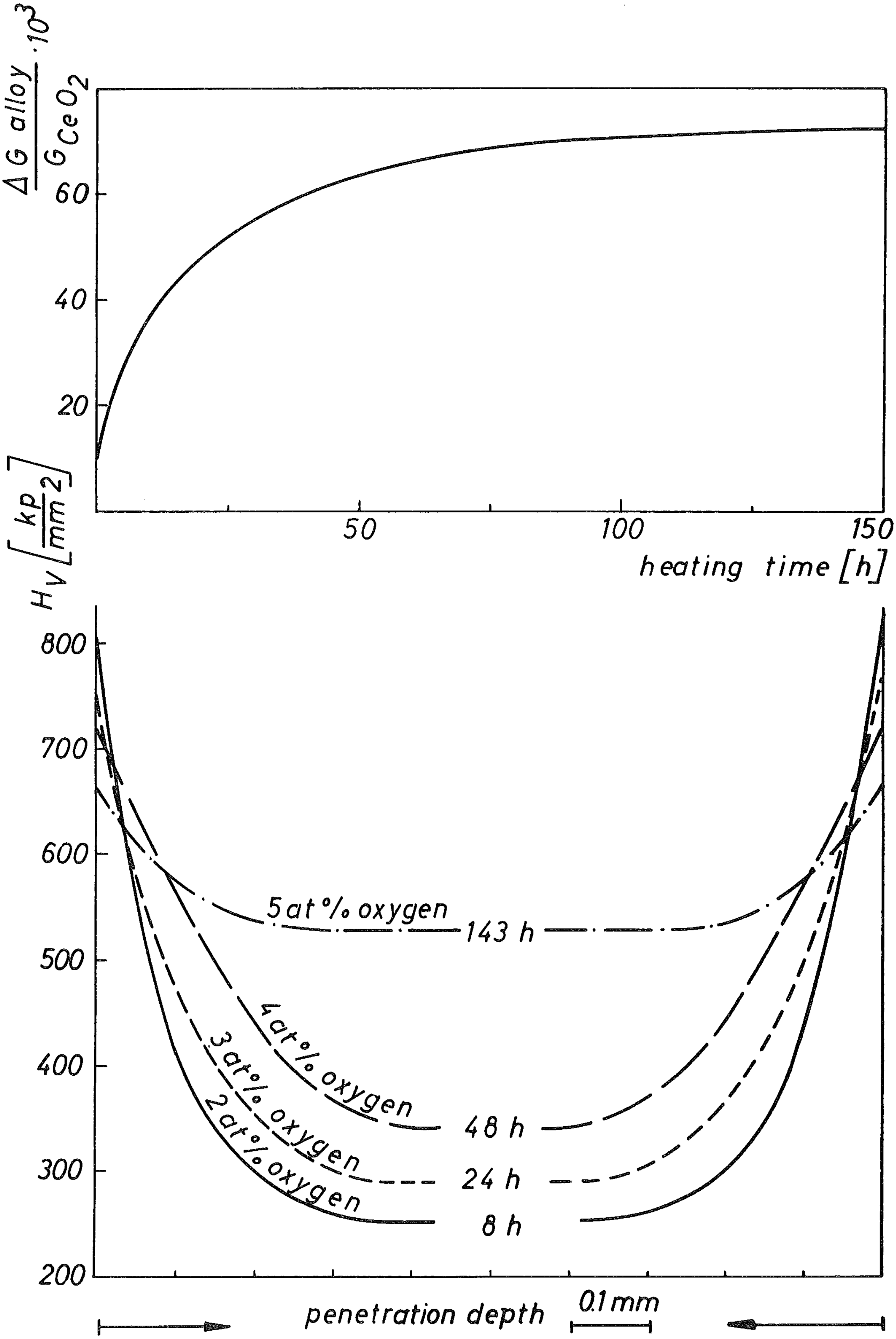

Fig. 3 Increase in weight as function of heating time and hardness profiles after various heating periods of a V3Ti1Si alloy disk, oxidized by CeO_2 powder at 800°C in argon atmosphere with 10 vpm hydrogen.